The Cryosphere

Discussions

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Interactive comment on "Dynamics of ionic species in Svalbard annual snow: the effects of rain event and melting" *by* Elena Barbaro et al.

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General Comments: R: This study conducted a series of snow pit chemistry measurements through the spring season in Svalbard with the goal of determining the behaviour of snowpack ionic species under the influence of melt and rainfall. The authors present a unique and very comprehensive dataset showing the seasonal-scale evolution of snowpack chemistry in relation to melt and meteorology. The dataset presented is valuable to our understanding of melt and rain processes and snowpack chemistry and is worthy of being published in a journal such as The Cryosphere. I also commend the authors on the study design and the huge amount of work required to undertake this study. However, as a manuscript, this paper has several major problems and is not yet suitable for publication. First, the paper contains many errors throughout the

manuscript that make the results and the quality of the interpretations very difficult to assess. Figures are referenced incorrectly (or not at all), there are many typos, problems with tense and pluralization and sections of informal or unpolished writing.

A: Thanks for all suggestions included in this referee's comment, we modified the manuscript in order to correct several errors and the figure numbers. We completely revised the manuscript.

R: While I have confidence in the data themselves, the statistical interpretations of the data were poorly described and were seldom justified by the authors. It is not clear that any of the results or discussion added any insight other than what would be immediately apparent by simply viewing the data.

A: We expanded the description of the statistical methodology adopted and also added more details in the interpretation of the results. See also our response to your question about the description of the statistical approach that you will find some pages later in this reply letter. Although we agree that a careful and expert view of the data plots may identify most of the effects reported in our analyses, we also think that it is important to quantify the amount of such effects using a proper statistical method. Moreover, there are some doubtful situations where our analyses were used to confirm the significance of the effects of the melting and rain events on the concentrations. We agree with the referee that these results are quite hard to explain, but the understanding of the dynamics of ionic species in snow, especially during specific events, is fundamental. These elements\species are used in paleoclimatic studies but also the release of specific ionic compound, such as nitrate, could have a direct consequence on the vegetative phase of the ground under the snow pack as well microbiological community. Understand the complex process is fundamental for several aspect not only connect with paleoclimate. Papers and research published on this topics try to simply the mechanism evaluating only the macro changes however this experiment bring new light on the complexity of the snow pack system and the chemical diffusion when liquid water Is present. The unique dataset presented will be available for implement snow diffusion models.

R: The discussion seems to be an extension of the results, describing the changes in snowpack chemical properties without providing much insight into the mechanisms and processes at play. Aside from a very discrete section on elution sequence, there were insufficient references or context. The few conclusions that the study draws, such as the elution sequence and the effects of the rain events, are not necessarily well-supported by the data (see specific comments). As it stands currently, this work would be most suitable for a data publication (on the Arctic Data Center, Pangaea or other repositories). Improving the manuscript as it stands would involve bringing in a wider variety of literature – particularly on chemical properties and behavior of ions. I would recommend a more thorough use of meteorological data that potentially includes back trajectory modeling or a comparison of the results with reanalysis products. Many of the problems can be fixed relatively easily with more thorough explanations and clearer writing. I hope that the authors proceed with publishing these results in some form as they represent a tremendous effort and an impressive dataset.

A: The data will be available upon request since the dataset will be too large and complex to be deposit in an on-line data access system with only text explanation.

Specific Comments:

R: I have not made an exhaustive list of mistakes and typos, but some are listed here in addition to specific scientific comments.

A: Thanks to referee, we corrected all suggested mistakes and we checked the entire manuscript to avoid inaccuracy or typos.

R: Line 26: Also Denali and Logan ice cores have very little/no melt. Consider rephrasing to "Nearly all ice core archives from the Arctic and middle latitudes, aside from very high elevation sites in Greenland and the North Pacific, are strongly influenced. . ."

A: Thanks for the suggestion. We have modified as follows: "Nearly all ice core archives from the Arctic and middle latitudes (such as the Alps), aside from very high elevation

sites in Greenland and the North Pacific, are strongly influenced by melting processes, able to modify the original chemical signal of the annual snowfall."

R: Line 28: "in the higher ice cap" - do you mean at higher elevations on ice caps in general? Or do you mean higher latitudes? Or are you referring to a specific ice cap?

A: As suggested by referee 1, we clarified as follows: "In the last decades, the increase of the average Arctic temperature has caused and enhanced surface snow melting at higher elevations on ice caps, especially in the Svalbard Archipelago".

R: Line 50: Should be "Dansgaard et al." – at least according you your references on line 570.

A: We corrected the mistake.

R: Line 53: "For example", not "For examples"

A: Done

R: Lines 50-65: I think there should be some acknowledgement that while the interpretations listed for each chemical compound listed are commonly used, there is still considerable variation in what each of these proxies mean among sites and a host of factors influencing each of these chemicals.

A: This paper is not focused on the deep discussion of the reliability of the different tracer in ice cores. In the introduction, we want to mention the chemical species, compounds or elements that are commonly used in paleclimate reconstruction. They are used as tracers and not proxy since some aspect of their source, transport and deposition is not always an easy task to decouple. The aim of the paper is to investigate the behaviour of specific ionic species in annual snow pack, to produce a daily picture of their behaviour. Several papers have been published, discussing this argument and giving an elution sequence based on their data. However, our results suggest that the elution sequence is not constant but depends from many parameter linked with the snow physical characteristic. The novelty of our approach is that glaciological

interpretations are driven by statistical quantification of the effects due to the melting and rain events.

R: Line 71: Change to either "over glaciers" or "over the glacier".

A: Done. We used "over glaciers"

R: Line 74: Higher altitudes or latitudes or both?

A: We modified with "higher altitudes".

R: Line 78: change to "dependent"

A: Done

R:Line 99-111: Very good summary of this project

A: Thanks

R: Lines 106-107: More details are required here. Did you drill a new 100 cm ice core each day and place the ice in a continuous melter system in order to measure physical properties? Why didn't you also sample chemistry if you are going through all this effort? If I am misunderstanding, then more clarification would be helpful.

A: All specific details were reported in the "Experimental Section" but, as suggested by the referee, we clarify the experiment as follows: "The upper 100 cm of the annual snowpack of the Austre Brøggerbreen glacier (Spitsbergen, Svalbard Archipelago) was dug daily manually using aluminium shovel from 27th March to 31st May 2015. The exposed snow wall was sampled using polyethylene precleaned tubes with a depth resolution of 10 cm. Then, the snow samples were processed under the laminar flow bench at Dirigibile Italia Arctic Station (Ny-Ålesund) to minimize possible external contamination and transported to Italy for analysis."

R: Lines 118-122: Are these statistics for Ny-Alesund or for your study site? If for Ny-Alesund, how much difference would you except in temperatures at your study site that

those you report here, if any?

A:Refer to next answer.

R: Lines 195: It is likely that the orography of the ice cap, the 270 meters of elevation difference and the albedo differences will also lead to differences in temperature between the station and the field site.

A: We agree with the referee, the measurements derived from the NyA AWS are not fully representative of the temperature at 270 m a.s.l.. Since no operative weather station are available on the glacier and in particular on the sampling site, we used the data available from NyA. The data can be corrected by a factor of $0.65°C\backslash100$ m, value often used in meteorology in adiabatic atmospheric condition. To estimate the temperature in our sampling location, the temperature determined in NyA should be decreased of $1.76°C$. Correcting the atmospheric data recorded in NyA, the interpretation will not change since the two rain on snow events recorded from January to April are characterized by temperature up to $3\backslash4°C$ positive. Anyway the text has been improved to be more clear.

R: Lines 143-149: This section is presented well.

A: Thanks

Lines 248-249: Why did you choose these sampling intervals?

A: To clarify how we chose the interval, we modified the manuscript as follows: For the biogenic ions we chosen to split the snow pack in three different layers: 1) the surface layer (10-20 cm) more affected by the wet\dry deposition derived by biological bloom during the period of the experiment; 2) the intermediate level (30-50 cm) to evaluate the possible diffusion of the deposited compounds into the snow pack (until the hard layers detected at 50 cm) and 3) the lower level as background and below the hard layer detect at 50 cm depth. Regarding the other ions we decided to split the snow pack into four layers mainly identify by the snow physical proprieties. The ions, included in this

group, are not directly linked with the biological bloom and can be deposited during the entire snow pack formation. For this reason, the layer division for these species was chosen using the physical snow proprieties at the beginning of the experiment. A layer characterized by soft snow (Hardness index 1 and 2) was detected from 10 to 40 cm depth, and hard layer (Hardness index 4 to 5) at 50 cm depth, and another ice layer at 90 cm depth that divide the lower snow pack into the layer include between 60 and 90 cm depth and at 100 cm depth (Figure 2, discussed later).

R: Lines 274: You reference Fig. 2, but these data are shown in Fig. 1. Fig. 1: It would be helpful and more quantitative to show the air temperature as a line graph instead of, or in addition to the colorscale displayed in Fig. 1B.

A: Thanks to the referee 1. We corrected the mistake. Fig. 1 was modified as suggested and the air temperature is now reported as a line graph. As suggested by referee 2, we modified also the colours to clarify the figure.

R: Lines 280-282: If you don't use the data from 50 cm depth after Apr. 18, then it should be removed from Figure 1. Currently it is by far the most striking feature in Fig. 1A and misleading if you think the data are unrealistic because the sensor was broken.

A: The sensor used to measure the liquid water content are sensors commonly used to measure soil humidity. Is likely that the sensor at 50 cm also after its repairing might have suffered of a bias since the sensor were not calibrate after substitution. However, the sensor seems working since record the enhancement LWC in the snow pack during the melting phase in agreement with the other two calibrated sensors installed at 25 and 75 cm depth. Considering that a -10°C no liquid water can exist, we used the measurements during this day to identify the bias on the sensor and we corrected the dataset data. Thanks to the referee for the precious suggestion.

R: Lines 283-284: You say there was no liquid water was detected at the 75 cm depth, but in the next sentence you say that there was liquid water at 75 cm after May 26. These statements should be reconciled.

A: As suggested by referee, we modified as follows: "No liquid water has been detected at 75 cm depth during the rain event instead, during the melting phase, the LWC increased through the entire snow column and finally reached the bottom part of our measured profile at 75 cm on the 26th of May. The constant increase of LWC is also consistent with the propagation of the heat wave through the snowpack (Fig. 1)."

R: Lines 288-302: Since this section essentially describes Fig. S1, I would either move this section to the supplement or move Fig. S1 into the main body of the paper.

A: As suggested by reviewer 1, we moved the Fig. S1 in the main manuscript. We checked all figure numbers and corrected all mistakes.

R: Line 314: What do you mean by "considering both the literature"?

A: We removed "both".

R: Line 321: There is no figure 4. Do you mean Fig. 3?

A: We checked all figure numbers and corrected all mistakes.

R: Line 322-327: These different concentration levels do not stand out to me for most of the plots in Figure 2 and Figure 3 (referenced as Fig.4). How were they chosen? It is also not clear yet, why it is necessary to group data from 10 depth levels into either 3 or 4 depth levels. This is especially true given that the authors just states on lines 318-320 that many of these ions have multiple sources, so it may not make sense to impose differential groupings on the data.

A: We clarified the main reason of this simplification as follows: "To simplify the huge dataset and to better understand the processes occurred in snow wall, three different concentration levels can be distinguished for biogenic ions (MSA, NO3-, C2 and C5) at 10-20 cm, 30-50 cm and 60-100 cm while four concentration levels can be identified for other ions at 10-40 cm, 50 cm, 60-90 cm and 100 cm. These layers were defined by considering the different ion sources and by evaluating the profiles reported in Fig. 3 and 4."

R: Figs. 2-3: This is a nice way to represent the data. It is a very impressive data set.
A: We can confirm that a huge work was carried out to sample, analyze and especially rationalize the dataset.

R: Lines 349: To me, it looks like the decrease is only apparent at 50 cm. Is there a statistically significant decrease anywhere else? Lines 349-350: There is no Table S2. Do you mean Table 2? Or Table 1?

A: Sorry, but we have reported the Table S2 in the Supplementary Material. It repots "Median concentrations of Br^-, K^+, Mg^{2+}, Ca^{2+}, Cl^-, Na^+, I^- and SO_4^{2-} by depth (10-40 cm, 50 cm, 60-90 cm and 100 cm) and phase (I: from 27th March to 16th April; II: from 17th April to 15th May; III: from 16th May to 31st May)." This sentence is included in the "Results" section and, here, we prefer to describe only the concentration results (Table S2). The discussion about the statistically significant changes was reported in the "Discussion" section, where we reported the p-values for each layer. The main conclusion of discussion about the changes in the snow wall is "The most influenced stratum was the 50 cm, due to the percolation of liquid water in vertical water channel where the ionic species were washed out in the deeper levels (below of 100 cm).".

R: Table 2: Just to clarify: are the values in table 2 calculated from the methods described in lines 252-261? In the figure 2 caption or in the results or discussion, it would be useful to be more explicit than you are when comparing changes in mean concentrations between phases 1, 2 and 3 of different chemicals.

A: Yes, the p-values of tables 1 and 2 are calculated as described in the "Statistical analysis". The caption of Fig. 3 (former Fig. 2) has been modified to clarify the different phases.

R: Line 353: What has led you to conclude that the increase in sulfate and iodine is biogenic? You haven't given any justification yet.

A: As suggested by referee, we added one sentence to clarify the biogenic source of

sulfate: "MSA and SO_2, which is further oxidized to SO_4^{2-}, are the main products of dimethyl sulfide (DMS), emitted during algal bloom (Gondwe et al., 2003)." The comparison of temporal trend between MSA and non-sea salt sulphate allowed to confirm the biogenic input of nss-SO_4^{2-}. Although for iodine other inorganic source might become relevant such as reaction of iodine compound with ozone over the sea water surface (Cuevas et al., 2018) is believed that biological emission are the main source for iodine in the polar areas (Cuevas et al., 2018; Saiz-lopez et al., 2007; Siaz-Lopez et al., 2012).

A: Line 359: At what contrast? Do you mean "in contrast", or are you talking about the difference between P2 and P3?

R: Sorry, we corrected as "In contrast".

A: Line 360: Do they all decrease significantly? It is not completely clear in Figure 3. What are the significance values and how did you calculate them? Are they in a table?

A: The ion concentrations of each phase was reported in the Table S2 of Supplementary Materials and we added this reference in the manuscript. The new description of the statistical analysis provides more details about how the significance values reported in the text and in Tables 1 and 2 are computed, see also our response to the following question.

R: Line 362: What statistical analysis? How were the p-values calculated? I assume this is using the procedures described in lines 252-261, but you need to remind us. Also, why were these methods chosen? How are they different than a more standard t-test or ANOVA? Have other studies used these methods?

A: We are sorry for the quality of presentation. We carefully revised the text to make clear that our discussion is based on the methods described (now with more details) in the section entitled "Statistical Analysis". The statistical analyses discussed in the paper are aimed at the identification of significant change of levels due to the melting

or the rain effects. In the paper was written that the statistical method used to identify such levels changes is "linear regression fitted using a robust M estimator". In fact, this is a simply a t-test with the change of level not estimated using the difference of the sample means before and after the event, but using a robust statistical procedure that is "resistant" to the presence of outliers. The choice of this form of robust t-test in place of the tradition t-test was necessary to avoid incorrect conclusions based on anomalous isolated observations. Statistical methods designed to be resistant to outliers, commonly referenced as "robust statistics", are an important domain of statistics and have been successful applied in a variety of fields. However, we are not aware of any previous use of robust statistical methods in glaciological studies similar to ours. The two academic statisticians who carried out the statistical analyses acknowledge that their description of the statistical methods used in the paper did not suit well the typical audience of the journal. For this reason, the description of the statistical analysis was rewritten adding more details about the employed methodology. We hope that the new description of the statistical methods contains all the elements necessary to evaluate our results.

R: Line 366: What are we supposed to see in these time series plots? I think they are very helpful and probably should be brought to the reader's attention earlier (for instance during the discussion of the shifts between P1, P2 and P3). Figure S4: There are two figures labeled Figure S4. One should be changed to Figure S5.

A: To avoid to create confusion we prefer to leave these figures in the supplementary information. These are the time series plots of averaged concentrations of non-biogenic and biogenic ions, that are produced to apply the statistical approach.

R: Line 371: Is this 80-100 cm depth on your normalized depth scale or relative to the surface at the time?

A: To clarify, we added "from the surface" after "between 80 and 100 cm of depth".

R: Line 376: This statement does not appear to be true for all of the ionic species. Are

you referring to only the ions in Figure 3 but not those in Figure 2? If so, why? And why do some species like chloride not show higher concentrations at depth?

A: As suggested by referee #1, we modified "ionic species" with "sea salt ions" reported in Figure 4. Moreover, we added an explanation about the Cl- behavior: "In contrast, chloride demonstrated a homogenous concentration through the snow strata, because chloride depletion can occur with the HClgas formation, with consequent mobilization in porous snow strata (De Angelis and Legrand, 1995)."

R: Line 383: Do you mean that there is ice free ocean south of Svalbard? Please correct this sentence to clarify and fix the grammatical errors.

A: We tried to clarify the concept as follows: "During the same period, sulphate and iodide (Fig. 3) had a similar profile than sea salt ions with the higher concentrations in the lower strata. These high concentrations can be due to the deposition by two rain events occurred in January and February of 2015. These rain events are mainly caused by warm air mass enriched with marine-related elements originated in the ice free ocean surface in southern of Svalbard (Moore, 2016; Rinke et al., 2017)."

R: Lines 379-385: If I understand this section correctly, you argue that that the rain events are from open water areas further to the south, which you infer will have higher ion concentrations. Do you have any data to support this assumption or are there any other studies you can reference that have led you to this conclusion. Since you know the dates of snow and rainfall, and you have been sampling ion concentrations in surface snow, I think you could test this hypothesis with the data in hand. There are a wide variety of tools that can constrain the moisture sources of storms at specific dates. I recommend you further investigate these assumptions using the data you have collected, perhaps combined with back-trajectory modeling to support this discussion.

A: As suggested by referee, we added to the Supplementary material the Figure S6, which reported the back-trajectories related to the two rain events of January and February 2015. To confirm our hypothesis, we modified the paragraph in the

manuscript as follows: "These high concentrations can be due to the deposition by two rain events occurred in January and February of 2015. These rain events are mainly caused by warm air mass enriched with marine-related elements originated in the ice free ocean surface in southern of Svalbard (Moore, 2016; Rinke et al., 2017), as demonstrate by back-trajectories calculated for these two rain events (Fig. S6)"

R: Line 385-387: It sounds like you are saying that snow = lower concentrations and melt = higher concentrations. This is not necessarily true. Snowfall events can have extremely varied ion concentrations, depending on the source and trajectory of the air mass. And melt can enrich some areas of the snow and dilute other areas. If I have misinterpreted this sentence, then please clarify.

A: This sentence was connected with the previous section where we discussed the presence of high concentration in the lower strata. To avoid confusion, we prefer to remove it.

R: Line 400: Change to "temperature".

A: Done

R: Line 404: What statistical approach? Please give details about what you actually did, quantitatively.

A: We are sorry for the quality of presentation. We carefully revised the text to make clear that our discussion is based on the methods described (now with more details) in the section entitled "Statistical Analysis".

R: Lines 410-420: I'm not sure this is a good way to define the elution sequences among a group of ions. You may have a species with a very low magnitude of elution that is still statistically significant or a high magnitude of elution that is not significant. Just because one ion has a more favorable p value, doesn't necessary mean that that ion elutes first or most strongly. I appreciate the effort involved in sampling snowpits every day, but you do not have a huge number of samples, they are all within a single

year and they are affected not just by melt, but many other things as well. Finally, since I don't even know what test you are doing to calculate these p values, I don't know what they mean physically.

A: As explained in the revised section "Statistical Analysis" we define the elution sentences on the basis of the t statistics that measure the "standardized" amount of change in the week subsequent to melting or rain event. The standardization implicit in the t-statistics is needed to compare ions measured on quite different scales. The p-values reported in the paper are in one-to-one correspondence with the absolute values of the t statistics and provide an alternative way to summarize the effects of the two events in terms of statistical significance. Since the amount of data is limited and we want to avoid over-interpretation of small differences in the t-statistics that are likely insignificant, then we followed the standard practice in statistics of declaring effects as highly significant, significant or weakly significant accordingly to different levels of the p-values.

R: Line 423: Why would bromide have a positive level shift? How does this fit with your arguments?

A: During spring time, Br can be also emitted from the sea ice as BrO through the mechanism of bromine explosion. Bromine explosion over sea ice can lead to an enrichment of Bromine compare to the sea water abundance in the snow deposition causing and enhancement of Br in the snow pack. For example, in the Greenland plateau the Br can be 20 times higher compared to the sea water abundance. It is likely that during the rain event part of the gas phase bromine present over Svalbard have deposited into the snow pack causing the increase of concentration.

R: Line 425: How do you know this? It doesn't look like you have made any measurements below 100 cm.

A: This is our hypothesis but further investigations are needed to confirm it. For this reason, we modified the manuscript as follows: "The main reason for the general de-

crease in the concentrations after the rain event may be linked to the presence of liquid water with percolation of ionic compounds to deeper levels (below 100 cm of depth). Further investigations are necessary to confirm this hypothesis."

R: Line 432: Why do you think this? Is this just speculation? Or are there other studies that have shown this? This could be interesting, but you need to back up this claim with a more thorough and fully referenced description of the physical mechanisms you infer.

A: "$Br-$ and SO_42- showed a positive level shift in the upper stratum (10-40 cm), meaning an increase of concentrations after a rain event. For $Br-$, this effect is probably due to atmospheric wash-out effect (Spolaor et al., 2019) of the wet deposition of the gas-phase of bromine emitted from sea ice during spring around Svalbard. Regarding sulphur compounds, an extra source of nss-SO_4 might undergo a transport from lower latitude (Fig. S3) causing a slight sulphate increase during the rain events in upper snow pack (Fig. 3 and 4, Table 2)."

R: Line 444: Figure 2 only goes as deep as 100 cm, so how do you know this? There is no Figure 4.

A: We agree with referee#1 and some mistakes about the figure numbering created confusion. We corrected the figure numbers and we introduce a "probable" because we hypothesized that "The concentration of the majority of ions decreased during the melting due to probable relocation of ionic species from above to below the 100 cm stratum (Fig. 3 and 4)."

R: Line 449: Why do you assume a continuous input of biogenic compounds, but not of saline compounds? Why are the saline ions depleted by melt while the biogenic ions appear to be unaffected? What about the chemistry of these ions would be consistent with your data?

A: As reported in the manuscript, we assume that the increase the biogenic com-

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pounds concentration in May (during the melting period) was likely due to the input of atmospheric deposition because in this period the marine biological primary production occurred and the emission of these species from the sea improved. To clarify the concept, we modified the manuscript as follows: "The increase in concentrations of biogenic compounds during the melting period is likely due to a continuous input of these compounds from atmospheric deposition onto the snowpack, because marine biological primary production increased in this period with the consequent increase in the emission of these compounds."

R: Line 456: This paragraph is very full of typos and grammatical errors and is very hard to interpret.

A: Sorry for the mistakes, we corrected the paragraph as follows: "Table 3 summarizes the sequence of preferential elution for each stratum related to rain and melting events. The comparison with previous studies (Table 3) highlighted the complexity of the main goal of this research. The first investigation about the elution sequence was published by Johannessen et al. (1977), and they reported that 50-80% of the solute species were eluted in the first 30% of melt water (fractionation), following this order: $NH4+>$ $Cl-> Na+$. Several other studies were performed in the natural field, highlighted an important deviation from laboratory experiments, models and theories."

R: Line 499: What statistical approach?

A: We are sorry for the quality of presentation. We revise the text of the conclusion to make clear that the conclusions are based on the methods described in the section entitled "Statistical Analysis".